Raman Scattering in Ionic Conducting $Li_2B_4O_7$ Crystals at High Temperatures

V.N. Moiseyenko[1], M.P. Dergachov[1] and Ya.V. Burak[2]

[1] Physics Department, Dniepropetrovsk National University, 13 Naukova St., 49050 Dniepropetrovsk, Ukraine, e-mail: optic@ff.dsu.dp.ua
[2] Institute of Physical Optics, 23 Dragomanov St., 79005 Lviv, Ukraine, e-mail: burak@ifo.lviv.ua

Abstract

Raman spectra of isotopically substituted $Li_2B_4O_7$ (LB4) crystals have been measured within a wide temperature region (290–1040 K). Temperature dependences of the parameters of vibrational modes with participation of lithium ion have been analyzed. The character of temperature dependences of the frequency and the damping constant of these modes testifies disordering of lithium sublattice and a possibility of order-disorder phase transition in the vicinity of 750 K. Resonant and anharmonic interaction effects have been found to determine spectral intensity distribution in the Raman spectra of LB4 crystals at high temperatures. The possibility of appearance of lithium plasmon vibration in the Raman spectra has been discussed.

Introduction

Numerous works on different physical properties of lithium tetraborate crystals $Li_2B_4O_7$ (LB4) point to promising possibilities for applications of these materials in acoustoelectronic devices [1,2], ultra-violet solid state lasers [3,4] and dosimetry [5]. Owing to high values of conductivity [6], their use in solid state power sources is not excluded, too. Efficiency of the applications of LB4 crystals in functional electronic devices is determined in many respects by thermal stability of their physical properties and absence of fatigue during the operation period.

The analysis of the results obtained in the works [1,2,6–12] allows one to mark out three temperature intervals (370–410, 500–700 and 750–900 K), where there are anomalies of physical properties of LB4 crystals. As a rule, the observed anomalies are connected with changes in the movement parameters of lithium ions and intensification of their migration [7–9]. The assumption [1] about the existence of phase transition in the 370–410 K interval has not been proven by later works [2,10,11]. The data on the phase transitions for the temperatures higher than 750 K are contradictory. So, the temperature dependence of nonlinear optical coefficient d_{31} does not prove a presence of phase transitions till 870 K [11]. On the other hand, frequency-independent maxima of the dielectric parameters ε_{11} and ε_{33} observed at temperatures higher than 780 K [1] point to availability of a phase transition. High-temperature anomalies in the elastic and quasielastic light scattering observed in the study [12] have been associated with the order-disorder phase transition ($T_c \approx 790$ K), which is due to lithium sublattice melting. As far as the authors know, only review Raman spectra of

LB4 crystals are available in the literature for the high-temperature region [13]. The results of these studies do not exclude a possibility of phase transition somewhere at 700–900 K. None detailed studies in the region of vibrations with the participation of Li$^+$ ion (100–500 cm^{-1} [14–16]) have been performed so far.

The aim of this work is to obtain experimental data on the movement characteristics for Li$^+$ ions and the possibility of order-disorder phase transition at the high temperatures, as well as to clear up the interpretation of vibrational spectrum for the LB4 within 50–550 cm^{-1} region.

Experimental

Measurements were performed for the LB4 single crystals with different contents of lithium isotopes: LB4-7-10 (^{7}Li – 96 % and ^{10}B–97.3 %) and LB4-6-10 (^{6}Li – 95% and ^{10}B – 97.3 %). The samples were rectangular parallelepipeds, with the edges oriented along crystallographic directions [100], [010] and [001]. Raman spectra regions 50–300 and 440–550 cm^{-1} were studied for these samples in the X(ZZ)Y and X(ZX)Y scattering geometries, corresponding to A$_1$(TO) and E(TO+LO) phonon symmetries, respectively. In order to investigate non-polar vibrational modes, the LB4-7-10 sample with the facets rotated by 45^0 around [001] direction was used. Such the orientation allowed us measuring the Raman spectra in the X$^/$(Y$^/$Y$^/$)Z and X$^/$(Y$^/$X$^/$)Z geometries that correspond respectively to A$_1$(IO)+B$_2$ and B$_1$ phonon symmetries.

Raman spectra were excited by the radiation of second optical harmonic of Nd^{3+}:YAG laser, (the basic wavelength of 532 nm and the mean radiation power of 150 mW). The spectrum of scattered radiation was analyzed with double monochromator DFS-12 and recorded with the aid of single-channel photon counting system based on cooled FEU-79 photomultiplier (the accumulation time 5 s). The spectral width of monochromator slits was 2 cm^{-1}.

Heating of samples was performed using an air resistance furnace.

Results and discussion

The spectra obtained by us are shown in Fig. 1 and 2. As mentioned above, a great number of Raman lines observed in 100–500 cm^{-1} region is caused by the vibrations with participation of lithium ions. This fact is proven by a high-frequency shift of maxima of these lines after substituting ^{7}Li for ^{6}Li. Such the shifts have been observed in both the paper [14] and our measurements (see the spectra at T = 290 K in Fig. 1a). The reason for the difference between the experimental values of shifts and those calculated in framework of harmonic approximation is an intricate character of these vibrations, which are due to 'mixed' motion of boron-oxygen groups and Li$^+$ ions [15]. The analysis of the data obtained in [14] allows us to assign such the Raman lines to the vibrations with Li$^+$ ion participation: 152, 256, 296, 336 and 491 cm^{-1} (A$_1$(TO) phonon symmetry), 207 and 242 cm^{-1} (B$_1$), 207, 244 and 263 cm^{-1} (B$_2$) and 256 cm^{-1} (E(TO+LO)). All the frequencies are presented for the Raman spectra of LB4-7-10. As seen from Fig. 1 and 2, the majority of these lines are the most sensitive to increase of temperature. Temperature dependences of the parameters of vibrational modes have been determined by fitting the obtained spectra and using the function $J(\Omega, T)$:

$$J(\Omega,T) = [n(\Omega,T)+1] \times$$

$$\times \sum_{j=1}^{N} I_j \frac{\Omega \Omega_j^2 \gamma_j}{[\Omega_j^2 - \Omega^2]^2 + \Omega^2 \gamma_j^2} + B, \quad (1)$$

where I_j is the integral Raman line intensity, Ω_j and γ_j respectively the frequency and the damping constant for the j-th vibration, $n(\Omega, T)$ the Bose-Einstein factor, B the background level and N the number of lines in the Raman spectrum. When performing the fitting, the latest results [16] for the vibrational spectrum of LB4 have been taken into account. So, the intense band at 152 cm^{-1} in the A$_1$(TO) spectrum of
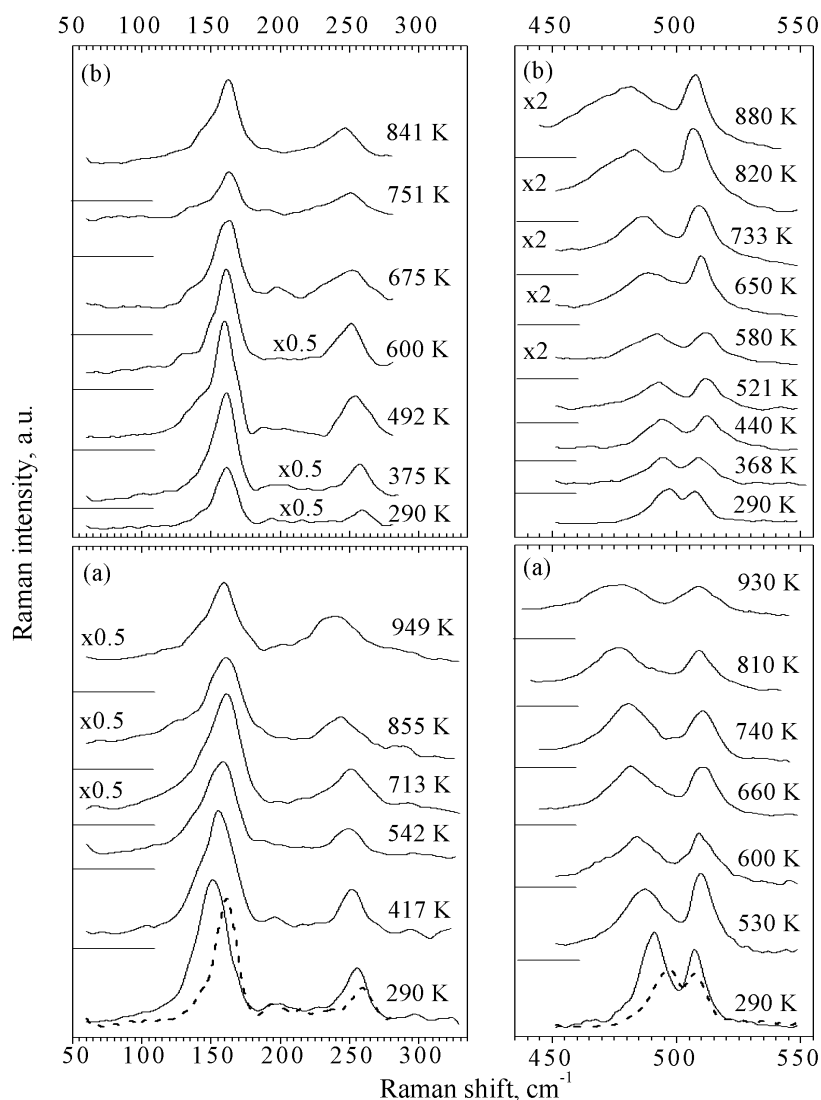
Fig. 1. Raman spectra of LB4-7-10 (a) and LB4-6-10 (b) crystals for the A_1(TO) phonon symmetry. Dashed line in plot (a) is the Raman spectrum for LB4-6-10 at 290 K represented for a comparison (see text).

LB4-7-10 and the band at 162 cm^{-1} of LB4-6-10 crystal have been presented as a sum of two Raman lines with the frequencies 147 and 157 cm^{-1}. The 50–300 cm^{-1} region of the E(TO+LO) spectrum at T = 300 K has been fitted using nine Raman lines. However, the attempts for obtaining accurate temperature dependences of the vibration parameters in this spectrum have failed because of a strong overlapping of the lines at higher temperatures (see Fig. 2c). Therefore the temperature dependences of the vibration frequencies $\Omega_j(T)$ have been determined only for the lines with clear spectral intensity maxima. The analysis

thus performed has enabled us marking out the two groups of vibrational modes, whose frequency shifts at increasing temperature are out of the measurement errors.

The frequencies of the modes referred to the first group are strongly lowered with increasing temperature. For the LB4-7-10 sample, these are the lines that correspond to the following frequencies: 256, 296 and 491 cm^{-1} – A_1(TO) phonon symmetry; 262 cm^{-1} – A_1(IO); 207 and 244 cm^{-1} – B_2; 207 см$^{-1}$ – B_1 and 256 cm^{-1} – E(TO+LO). The temperature dependences $\Omega_j(T)$ for a number of vibrations of this group are plotted in Fig. 3a and 4a. The

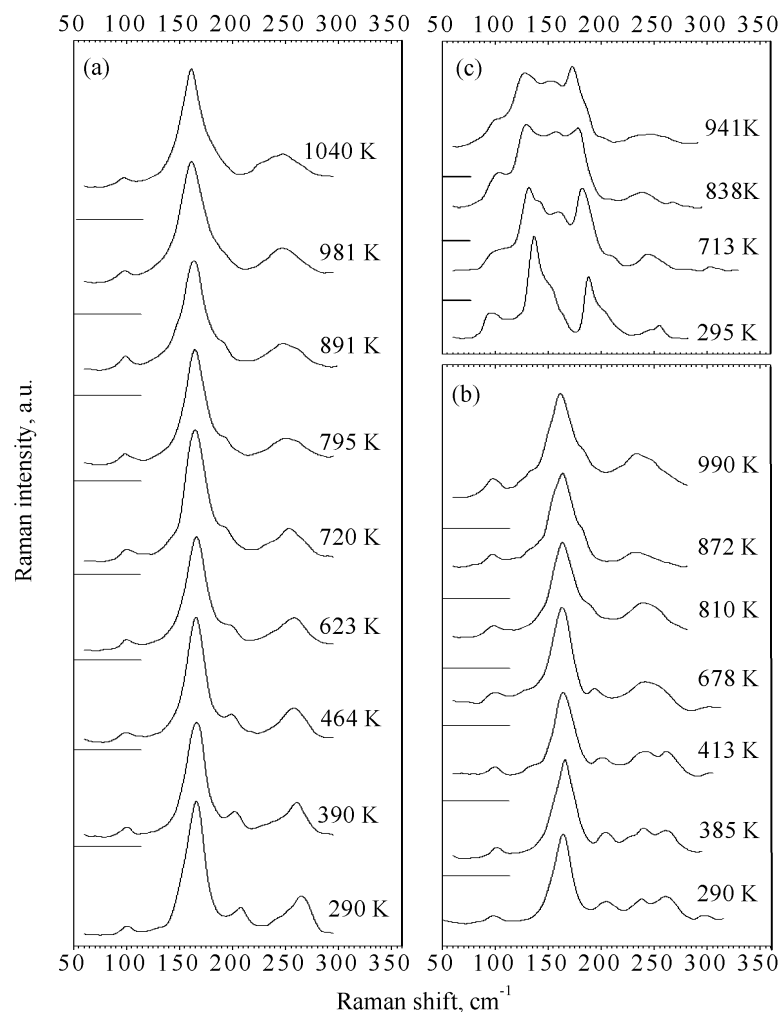**Fig. 2.** Raman spectra of LB4-7-10 crystal for the $A_1(lO)+B_2$(a), B_1(b) and E(TO+LO) (c) phonon symmetries.

frequency of these modes lowers by not less than 14 cm^{-1} when the temperature increases from 300 up to 1000 K. This is also accompanied by essential increase of the damping constant. The most typical dependences $\gamma_j(T)$ are presented in Fig. 4b for the $A_1(TO)$ modes located at 491 cm^{-1} (the case of LB4-7-10 crystals) and 496 cm^{-1} (LB4-6-10). The increase in the damping constant is known to be caused by anharmonicity of vibrations, crystal lattice disordering and defects available in crystals. Nonetheless, nonlinearity of the dependences plotted in Fig. 4 cannot be explained by anharmonic effects only [17]. Taking into account the assignment of the vibrations made above, one can conclude that the character of increase in the damping constant should rather testify disordering in the lithium

sublattice and point to possibility of order-disorder phase transition [18]. In case of ion hopping movement, which does not break the lattice symmetry, the temperature dependence of the damping constant $\gamma_j(T)$ of the j-th vibration is determined by the expression [19]

$$\gamma_j(T) = \gamma_0 \exp(-E_a / k_B T), \qquad (2)$$

where γ_0 denotes the temperature independent constant, E_a the movement activation energy and k_B the Boltzmann constant. As seen from Fig. 4b (insert), the dependence $\ln(\gamma_j/\gamma_0) = f(1/T)$ may be approximated by two linear regions, with a break in the vicinity of $T = 750$ K. This break shows a change in the movement activation energy. The E_a values calculated on the basis of Eq. (2) by averaging the experimental data are 0.023 ± 0.005 eV ($T < 750$ K) and 0.11 ± 0.03 eV

(T>750 К). The first value is close to the estimation of E_a (0.028 eV) obtained with the analysis of $\gamma_j(T)$ dependence for the A_1(LO) mode at 370 cm^{-1} [20]. The second one is smaller than the E_a value (0.23 eV) extracted from the temperature dependences of elastic and quasielastic light scattering parameters [12]. Beside of the damping constant increase, a nonlinear character of $\Omega_j(T)$ dependences in the region of 750–800 K should be pointed out, especially for the case of 496 cm^{-1} (see Fig. 4a). Such the behaviour of Raman line frequency has been already observed in the Raman spectra of LB4 in the vicinity of T_c = 235 K [20]. It has been interpreted as isomorphic phase transition with multiplication of elementary cell [21].

The second group mentioned above consists of Raman lines whose frequencies increase with heating the sample. These are the A_1(TO) modes at 152, 193 and 508 cm^{-1} and the E(TO+LO) mode at 95 cm^{-1} (Fig. 3b). The frequency increase for these modes occurs till the temperatures about 750–800 K. At further temperature increase, the frequency maximum is slightly lowered. As suggested in the study [14], a number of low-frequency Raman lines may be assigned to plasmon vibrations induced by longitudinal vibrations of the lithium ion density along [001] direction. The well-known dispersion law for the plasmon vibrations is as follows [22]:

$$\Omega_j^2(\mathbf{q}) = \Omega_p^2 + \alpha \mathbf{q}^2 /(N_{Li} M_{Li}), \qquad (3)$$

where $\Omega_p^2 = 4\pi N_{Li} e^2 /(M_{Li} \varepsilon_\infty)$ means the plasmon vibration frequency, α the coefficient that describes the back-moving elastic force in the system of particles, ε_∞ the high-frequency dielectric constant, M_{Li} the lithium ion mass and e the electron charge. The number of "free" Li^{+} ions at the given temperature is determined by the expression

$$N_{Li} = N \exp(-E_F / k_B T) + N_{Li}^{(0)}, \qquad (4)$$

where $N_{Li}^{(0)}$ is the concentration of the growth defects at the sites of lithium ions, N the

concentration of lithium ions in the crystal lattice (1.73×10^{22} cm^{-3}) and E_F the energy of formation of Frenkel defect. As seen from Eqs. (3) and (4), the increase of temperature should result in increasing concentration of the "free" ions and, consequently, shifting the plasmon frequency towards the high-frequency region. In order to verify numerically the hypothesis of the plasmon nature of some low-frequency modes, we have estimated the value of $N_{Li}^{(0)}$ (~ 10[20] cm^{-3}) on the basis of data of the conductivity measurements [6] and have calculated the lithium plasmon frequency with the aid of Eqs. (3) and (4) by varying the value of E_F in the range of 0.36–0.64 eV [9]. When using such the parameter values and neglecting the dispersion factor ($[\alpha \mathbf{q}^2 /(N_{Li} M_{Li})]/ \Omega_p^2 \sim 10^{-4}$), we have obtained that the highest frequency of the lithium plasmon vibrations could not be larger than 18 cm^{-1} at T = 300 K. As the temperature increases from 300 to 1000 K, the high-frequency shift of the plasmon frequency should not exceed 16 cm^{-1} for the value of $E_F = 0.36$ eV. Consideration of phonon-plasmon interaction effects [22] has not resulted in any essential changes of the plasmon frequency values. As seen from Fig. 1 and 2, the Raman spectra do not contain the lines with such significant high-frequency shifts. The earlier studies of the quasielastic light scattering spectra have not revealed the signs of the plasmons within the range of 5–30 cm^{-1} [12]. Thus, the frequency increase for the vibrations of the second group cannot be explained in terms of plasmon vibrations.

In spite of absence of direct facts testifying participation of Li^{+} in these vibrations [14,15], the observed anomalies (see Fig. 3b), in our opinion, may be connected with anharmonic effects caused by increasing vibration amplitude as the temperature is raised. First of all, the increase of the vibration amplitude for Li^{+}
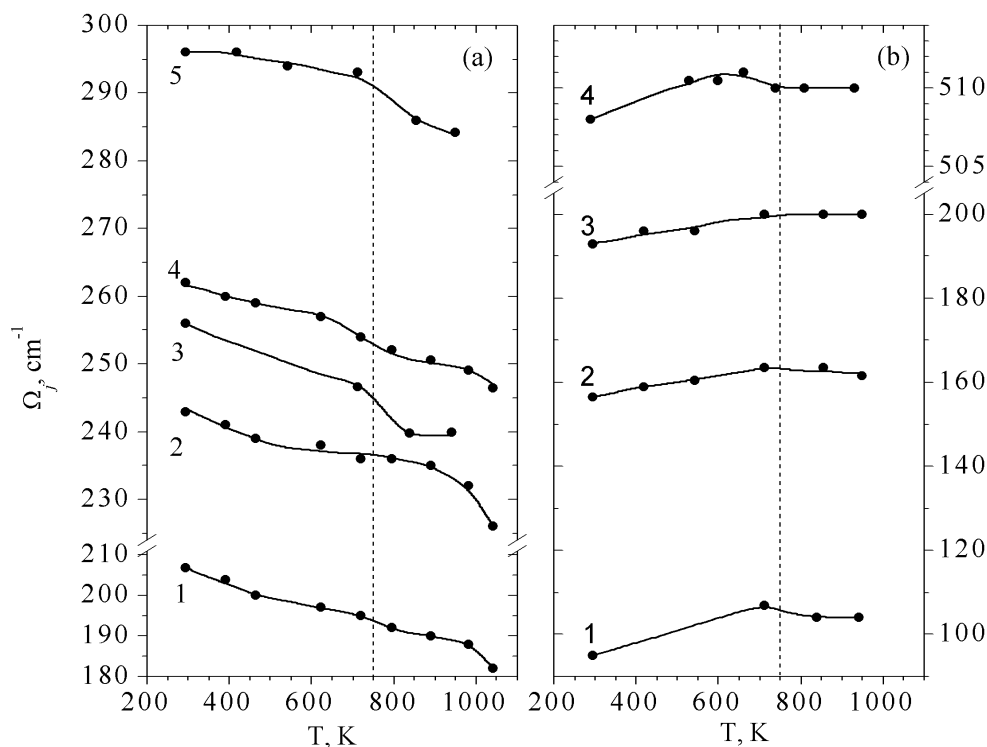
Fig. 3. Temperature dependences of frequencies for the following modes in LB4-7-10 crystal. Plot (a): 1 – 207 cm^{-1} (B$_1$), 2 – 244 cm^{-1} (B$_2$), 3 – 256 cm^{-1} (E(TO+LO)), 4 – 262 cm^{-1} (A$_1$(IO)) and 5 – 296 cm^{-1} (A$_1$(TO)). Plot (b): 1 – 95 cm^{-1} (E(TO+LO)), 2 – 157 cm^{-1} (A$_1$(TO)), 3 – 193 cm^{-1} (A$_1$(TO)) and 4 – 508 cm^{-1} (A$_1$(TO)).
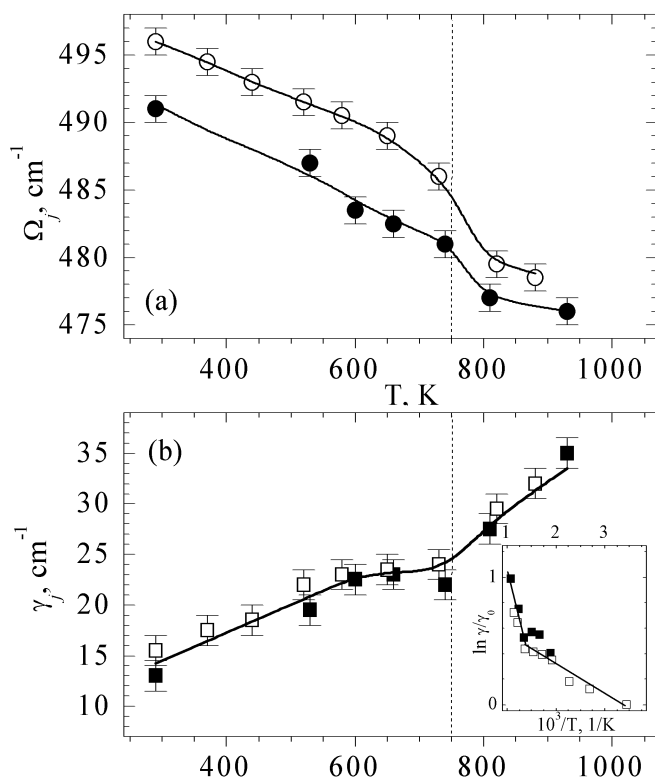

Fig. 4. Temperature dependences of frequencies (a) and damping constants (b) for the modes at 491 cm^{-1} (solid dots) and 496 cm^{-1} (open dots). The insertion shows the damping constant dependences on the semilogarithmic scale.

should be taken into account. As the temperature increases, the region of influence of lithium ion on the neighbouring atoms is enlarged. This process may be responsible for the high-frequency shift of these modes. At the temperatures higher than 750–800 K (i.e., at the

suggested transition into the state with lithium sublattice disordering), the influence of lithium ions on these vibrations becomes weaker, and their further temperature evolution is mostly determined by slow "softening" of boron-oxygen skeleton.

Besides the anomalies considered above, an asymmetry of the Raman lines at $152\,\text{cm}^{-1}$ (LB4-7-10) and $160\,\text{cm}^{-1}$ (LB4-6-10) has been detected in the A_1(TO) spectrum at temperatures higher than 400 K (see Fig. 1a and 1b). The observed changes in the spectral intensity distribution have been described by introducing one more vibrational mode at $126\,\text{cm}^{-1}$ (LB4-7-10) and $138\,\text{cm}^{-1}$ (LB4-6-10). The frequencies of these modes have very weak temperature dependence. The nature of this vibrational state is not clear. We do not exclude that the modes under discussion are present in the spectra at the room temperature. However, their appearance becomes more clear at higher temperatures, owing to transformation of vibrational spectrum due to the resonance interaction between the modes with close frequencies. Essential redistribution of the intensity in the E(TO+LO) spectrum (see Fig. 2c) can be also explained by the effects of resonance interactions of modes.

Conclusions

The analysis of the Raman spectra obtained for isotopically substituted LB4 crystals allows to assert that the character of temperature dependences of the frequency $\Omega_j(T)$ and damping constant $\gamma_j(T)$ for the vibrational modes is mainly determined by the intensity increase for the lithium ion migrations occurring at increasing temperature. The estimated values of the movement activation energy are quite agreeable to those presented in the earlier studies [8,12,20]. No significant isotopic substitution effects on the processes mentioned above have been detected. The anomalies in the $\Omega_j(T)$ and $\gamma_j(T)$ dependences observed for a number of Raman lines testify the influence of thermoactivation processes of lithium sublattice

disordering on the vibrational spectra of LB4, with a further realization of order-disorder phase transition within the region of 750–800 K. This temperature region agrees well with the one, in which the anomalies of other physical parameters of LB4 crystals have been observed [1,12].

The nature of the low-frequency vibrations ($\Omega_j \sim 100\,\text{cm}^{-1}$) has been found to be not associated with the lithium plasmon vibrations and the phonon-plasmon interaction effects. The majority of these vibrations are related to the lithium ion ones, being a part of translations and librations of the boron-oxygen groups.

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